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# Electronic Structure of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{V}$ Single Crystals, Comparison with Sintered Ceramics

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$\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG) single crystals doped with vanadium ions ( $\text{V}^{3+}$ ) were obtained by the Czochralski method. The X-ray photoelectron spectra of YAG:V annealed in reducing atmospheres:  $\text{H}_2$ , vacuum and  $\text{H}_2$  + vacuum are presented and compared with the spectra of the YAG ceramics. The X-ray photoelectron spectra showed that the vanadium dopant concentration in YAG:V crystals is lower than a nominal one. For the "as grown" YAG:2.8at.%V crystal vanadium exists in the mixed valence state. The increase in lattice parameters for the samples annealed in hydrogen was found.

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## 1. Introduction

YAG: $\text{V}^{3+}$  is one of the few known materials, which show a nonlinear absorption effect. Such materials are especially attractive for Q-switching operation to obtain high peak power optical pulses [1]. Recently the YAG ceramics were synthesized to replace the YAG single crystals. These ceramics, which are characterized with similar to the YAG single crystals optical properties, were obtained to increase the doping range, simplify technological process and lower costs. Moreover, there is possible obtaining of ceramics shapes with bigger size than single crystals grown by the Czochralski method [2]. X-ray photoelectron spectroscopy (XPS) was used to study the chemical composition and electronic structure of the YAG:V single crystals. For comparison the ceramics were investigated.

## 2. Experimental

Single crystals of YAG:V were grown with the use of the Czochralski method. The thermal system consisted of a 53 mm outer diameter, 50 mm high and 1.5 mm wall thickness iridium crucible, in passive iridium afterheater placed around the crucible top on the grog, and alumina heat shields around the afterheater. A charge material was prepared on base of high purity oxides:  $\text{Y}_2\text{O}_3$  (5.0N),  $\text{Al}_2\text{O}_3$  (5.0N) and  $\text{V}_2\text{O}_5$  (4.5N) as a dopant. The nominal concentration of the  $\text{V}^{5+}$  ions was 0.8 and 2.8 at.%. The growing atmosphere was pure nitrogen. The following conditions of the growth processes were applied: growth rate 0.6–1.2 mm/h; rotation rate 5–20 rpm; cooling after

growth — at least 24 h. The obtained single crystals up to 20 mm in diameter and 65–70 mm in length were free of macroscopic defects and inclusions of other phases. An example of the "as grown" single crystal is shown in Fig. 1.



Fig. 1. An "as grown" YAG:V single crystal obtained by the Czochralski method.

Each crystal was sliced into wafers of about 1 mm thickness. A wafer from a middle part of the crystals was used for examinations. The wafer of YAG:0.8at.%V was divided into four parts, which were annealed in reduction atmospheres: (1) in hydrogen, at 1200°C for 10 min; (2) in vacuum, at 1750°C for 5 h; (3) first in hydrogen at 1200°C for 10 min and next in vacuum, at 1750°C for 5 h. After annealing the samples were slowly cooled down to room temperature.

Besides the single crystals the YAG ceramics were obtained. Ammonium hydrogen carbonate was applied as precipitant for production of YAG nanopowders from so-

lution of nitrates. Powders were calcinated up to 1100°C, milled, mixed in proper proportions for solid state reaction synthesis, and densified by isostatic pressing at the pressure of 200 MPa. Powder compacts were sintered in vacuum ( $10^{-6}$  Tr) within the temperature range of 1700–1780°C and holding time up to 60 h. Several samples were prepared with 0.5% of tetraethyl orthosilicate (TEOS) as sintering aid.

The XPS spectra were obtained using a PHI 5700/660 Physical Electronics Photoelectron Spectrometer with monochromatized Al  $K_{\alpha}$  X-ray radiation (1486.6 eV). All measurements were performed on the crystal broken under UHV conditions of  $10^{-10}$  Tr. The binding energy was determined with reference to the C 1s component set at 284.6 eV. The Gaussian-Lorentzian functions were used to fit the XPS core level spectra [3, 4]. The lattice parameters of the YAG:V single crystals were studied at the room temperature using a four-circle KM4 diffractometer with graphite-monochromatized Mo  $K_{\alpha}$  radiation.

### 3. Results and discussion

Changes of the lattice parameters after annealing processes for the nominal YAG:0.8at.%V samples and pure stoichiometric YAG crystal were collected in Table I. The measurements show an increase in the lattice parameters for the YAG samples doped with V ions in comparison to the pure YAG crystal and another increase in lattice parameters for the samples annealed in hydrogen. It seems that annealing in vacuum does not change the lattice parameters.

TABLE I  
Lattice parameters of the YAG and different treatment of YAG:0.8at.%V single crystal.

Lattice parameters [Å]	
YAG single crystals	<i>a</i>
YAG stoichiometric “as grown” transparent	12.0050(6)
YAG:V “as grown”	12.0056(6)
YAG:V annealed in H <sub>2</sub>	12.0071(7)
YAG:V annealed in vacuum	12.0057(6)
YAG:V annealed in H <sub>2</sub> and vacuum	12.0082(7)

The example XPS spectrum of the “as grown” YAG:2.8at.%V single crystal in a wide energy range is shown in Fig. 2. Table II shows the chemical composition, calculated using the XPS spectra for the YAG:V single crystals and YAG ceramics. All samples exhibited an increased amount of oxygen and yttrium and reduced amount of aluminum in relation to the nominal value. As in earlier measurements, lower content of aluminum ions and excess of oxygen ions for “as grown” YAG:Yb crystal was found [5]. The possible explanation is the presence of the YAG blocks separated by yttrium oxide layers. Similar type of structure is described in the literature as the Ruddlesden–Popper phases [6]. Moreover, the annealing

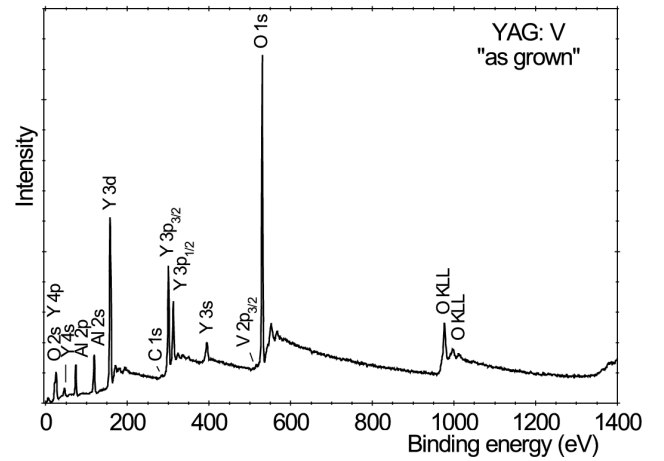


Fig. 2. The XPS spectrum in the wide energy range of the “as grown” YAG:2.8at.%V single crystal.

procedure did not remove the excess of oxygen markedly.

TABLE II  
Chemical composition of the YAG:V single crystals and YAG ceramics.

Chemical composition				
	Y	Al	O	V [at.%]
YAG single crystals				
YAG stoichiometric “as grown” transparent	3.01	5.01	11.98	
YAG:0.8at.%V “as grown”	3.12	4.72	12.16	
YAG:0.8at.%V annealed in H <sub>2</sub>	3.11	4.75	12.14	
YAG:0.8at.%V annealed in vacuum	3.12	4.80	12.08	
YAG:0.8at.%V annealed in H <sub>2</sub> and vacuum	3.12	4.79	12.09	
YAG:2.8at.%V “as grown”	3.07	4.80	12.13	0.71
YAG ceramics “as grown”				
YAG stoichiometric transparent	3.01	4.99	12.00	
YAG non-transparent	3.09	4.79	12.13	
YAG with 0.5% TEOS non-transparent	3.13	4.78	12.08	

The XPS studies showed for the all YAG:0.8at.%V crystal samples the amount of vanadium is below the limit of the sensitivity of the method. For the “as grown” YAG:2.8at.%V crystal the amount of vanadium is lower in relation to the nominal one. The vanadium 2p states are split due to spin-orbit interaction into two lines V 2p<sub>3/2</sub>–V 2p<sub>1/2</sub> with energy splitting  $\Delta = 7.6$  eV and intensity ratio  $I(2p_{3/2})/I(2p_{1/2}) = 2/1$  (Fig. 3). A deconvolution of the V 2p showed two components related to V<sup>3+</sup> and V<sup>5+</sup>. The first line (M) in V 2p<sub>3/2</sub> related to the V<sup>3+</sup> component was at 515.7 eV. Such binding energy

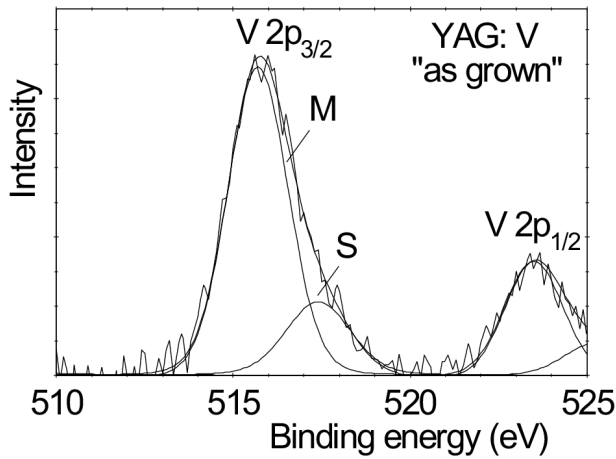


Fig. 3. The V 2p line of the “as grown” YAG:2.8at.%V single crystal.

was confirmed by XPS measurements of the V 2p line in  $V_2O_3$  [3]. The second line (S) related to the  $V^{5+}$  was at 517.4 eV as in  $V_2O_5$  [3]. The ratio of areas between additional (S) and main (M) lines was 0.27.

The Y 3d, Al 2p, and O 1s lines were deconvoluted after a background subtraction and example spectra were shown in Fig. 4. The Y 3d and Al 2p lines are decomposed into two lines split due to spin-orbit interactions: Y  $3d_{5/2}$ –Y  $3d_{3/2}$  with splitting energy  $\Delta = 2.02$  eV, the intensity ratio  $I(3d_{5/2})/I(3d_{3/2}) = 3/2$  and Al  $2p_{3/2}$ –Al  $2p_{1/2}$  with  $\Delta = 0.45$  eV,  $I(2p_{3/2})/I(2p_{1/2}) = 2/1$ . The binding energies of these elements are not significantly changed for all samples and they are approximately Y  $3d_{5/2} = 157.3$  eV, Y  $3d_{3/2} = 159.3$  eV, Al  $2p_{3/2} = 73.35$  eV, Al  $2p_{1/2} = 73.8$  eV and O 1s = 530.15 eV. The analysis of the O 1s lines shows that the intensity of the additional line at lower binding energy for the “as grown” crystal after annealing disappeared. This is caused by improvement of the crystal structure after the annealing process. The XPS lines for the samples annealed are narrower and better split and valence bands show less broadening towards the Fermi level suggesting less defects present in the structure. Moreover, in comparison with the YAG:V single crystals all XPS lines for the YAG ceramics are narrower and better split, even in comparison with annealed crystals. This indicates better quality of the crystal structure for ceramics.

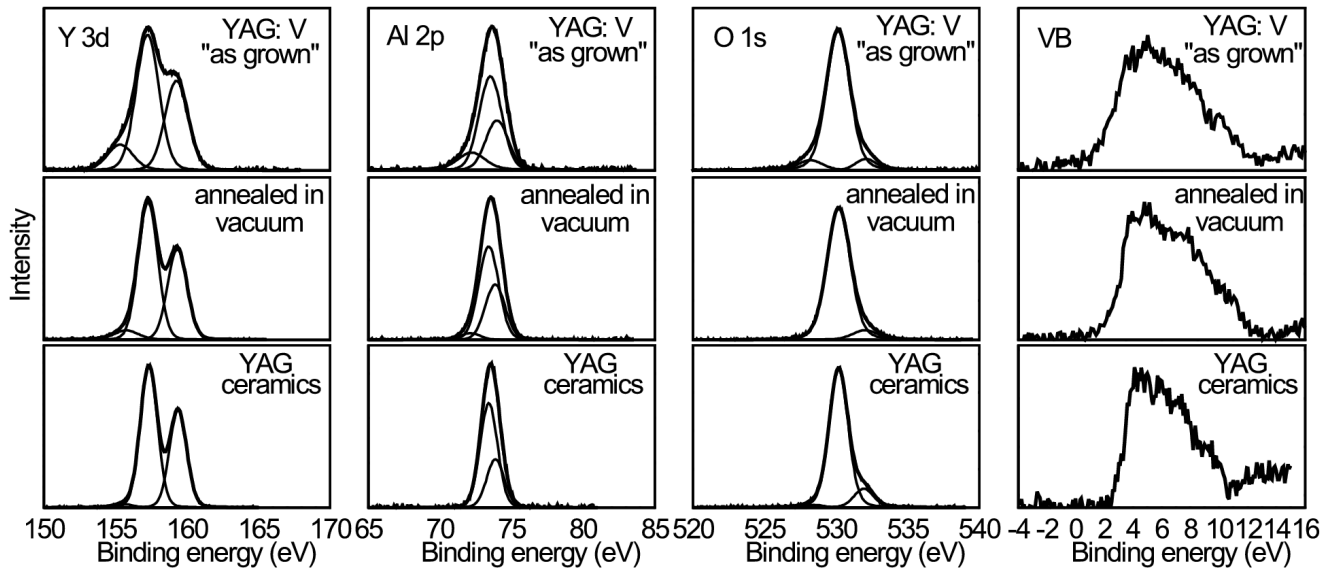


Fig. 4. The Y 3d, Al 2p, O 1s lines and valence bands of the YAG:0.8at.%V single crystal and YAG ceramics.

#### 4. Conclusions

- The aluminium deficiency, yttrium and oxygen excess for the all measured samples was found.
- The vanadium dopant in the “as grown” YAG:2.8at.%V crystal exists in the mixed valence state and was lower than a nominal one. The total

$V^{3+}$  and  $V^{5+}$  dopant concentration was determined as 0.7at.%.

- The amount of vanadium in the YAG:0.8at.%V crystal was below the limit of the sensitivity of the method.

- The lattice parameters changes for annealing in hydrogen were observed.

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